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Interim Protocol for the Automated Analysis of Semivolatile Organic Compounds by Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry (Journal Version)

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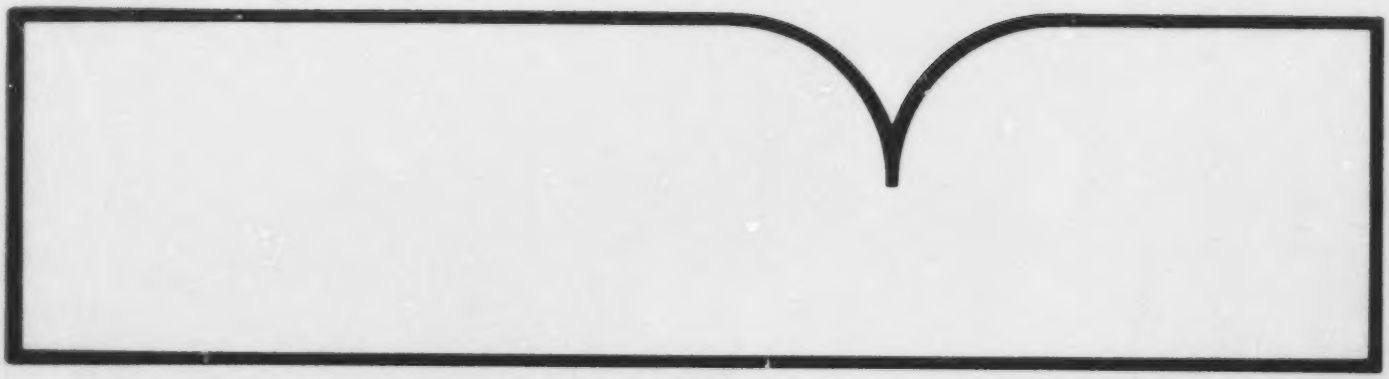

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16. ABSTRACT

The application of gas chromatography/Fourier transform infrared (GC/FT-IR) data to regulatory decisions requires, among other things, the availability of validated analytical protocols. Such protocols are necessary for the generation of reliable analytical data. A GC/FT-IR protocol is described which is applicable to the determination of semivolatile organic compounds in wastewater, soils, sediments, and solid wastes. The protocol is designed for the high-throughput automated analysis of multicomponent environmental and hazardous waste extracts. Wastewater analysis for semivolatile organic compounds is based upon the extraction of 1 L of sample with methylene chloride and the concentration of the extract to 1 mL. The analysis of the semivolatile fraction derived from solid waste analysis is based upon the extraction of 50 grams of sample and concentration of the sample extract to 1.0 mL. A gel permeation cleanup option is included to further purify those extracts which cannot be concentrated to the specified final volume. With the use of capillary GC/FT-IR techniques, wastewater identification limits of 150 to 400 ppb can be achieved with this method, while the corresponding identification limits for solid samples are 3 to 88 ppm. Automated packed-column GC/FT-IR identification limits are approximately a factor of five higher than the corresponding capillary GC/FT-IR values.

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Interim Protocol for the Automated Analysis of Semivolatile Organic Compounds by Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry*

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The application of gas chromatography/Fourier transform infrared (GC/FT-IR) data to regulatory decisions requires, among other things, the availability of validated analytical protocols. Such protocols are necessary for the generation of reliable analytical data. A GC/FT-IR protocol is described which is applicable to the determination of semivolatile organic compounds in wastewater, soils, sediments, and solid wastes. The protocol is designed for the high-throughput automated analysis of multicomponent environmental and hazardous waste extracts. Wastewater analysis for semivolatile organic compounds is based upon the extraction of 1 L of sample with methylene chloride and the concentration of the extract to 1 mL. The analysis of the semivolatile fraction derived from solid waste analysis is based upon the extraction of 50 grams of sample and concentration of the sample extract to 1.0 mL. A gel permeation cleanup option is included to further purify those extracts which cannot be concentrated to the specified final volume. With the use of capillary GC/FT-IR techniques, wastewater identification limits of 150 to 400 ppb can be achieved with this method, while the corresponding identification limits for solid samples are 3 to 88 ppm. Automated packed-column GC/FT-IR identification limits are approximately a factor of five higher than the corresponding capillary GC/FT-IR values. The most frequent obstacle to the achievement of these identification limits is expected to be the presence of large quantities of interfering high-boiling coextractants. These coextractants would raise the identification limits by preventing the concentration of extracts to the desired final volume, thereby necessitating gel permeation cleanup, and/or by decreasing the spectral signal-to-noise of GC-volatile analytes by raising the spectral background intensity.

Index Headings: **Analyses for environmental pollutants; Infrared; GC/FT-IR instrumentation.**

INTRODUCTION

The applicability of the gas chromatography/Fourier transform infrared (GC/FT-IR) spectrometic technique to the analysis of wastewater, soils, sediments, hazardous wastes, and diesel particulates has been demonstrated.[1-8] There is currently some disagreement concerning

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TABLE I. Contents of interim protocol.

1.0	Scope and Application
2.0	Summary of Method for GC/FT-IR Analysis
3.0	Safety
4.0	Interferences
5.0	Apparatus and Material
6.0	Reagents
7.0	Calibration Standards and Internal Standards
8.0	Extraction of Solid Samples (Base/Neutrals)
9.0	Sample Extraction (Acids)
10.0	Extract Cleanup and Calibration (Optional)
11.0	GPC Cleaned Extract Concentration
12.0	Extract Drying
13.0	Extract Concentration
14.0	Daily FT-IR Quality Assurance/Quality Control
15.0	Periodic FT-IR Quality Assurance/Quality Control
16.0	Initial FT-IR Quality Assurance/Quality Control
17.0	GC/FT-IR Extract Analysis
18.0	Quantitation

the sensitivity of the GC/FT-IR technique, with reported capillary sensitivity values ranging from 40[3] to 800[1] nanograms (ng). Much of this disagreement may be attributed to the use of different MCT detectors, different lightpipes, and different lightpipe temperatures. In addition, some researchers have reported sensitivity values which are based on *nominal* GC split ratios.[3] Shafer *et al.*[2] have noted that the choice of utilizing GC/FT-IR or GC/MS should be based on the relative information content, as well as the relative sensitivity of these two techniques. The implementation of recently proposed improvements in GC/FT-IR technology[9] promises to improve the sensitivity of this technique to the low nanogram range. This improved GC/FT-IR sensitivity range would be close to that currently in use for the analysis of unpurified methylene chloride environmental extracts by gas chromatography/mass spectrometry (GC/MS) techniques. The feasibility of the direct-linked GC/FT-IR/MS method for multicomponent analysis promises an economical solution to GC/FT-IR confirmation and supplementation of the GC/MS analytical method.[10–12] This economy will be realized through the availability of low-cost FT-IR and MS detectors and through the development of powerful computer software to process the large quantities of spectral data generated by the use of two detectors for every analytical run.

Before the use of GC/FT-IR or direct-linked GC/FT-IR/MS analysis for regulatory decisions becomes widely accepted by the academic, industrial, and governmental communities, validated protocols for their usage must be available. These protocols should be validated by procedures designated by the appropriate mechanisms within the scientific community. The Association of Official Analytical Chemists (AOAC) and American Society for Testing Materials (ASTM) provide such authority and both have proposed suitable validation procedures for analytical protocols.[13,14]

A GC/FT-IR protocol is described which is applicable to the routine workup and on-line analysis of environmental contaminants. The workup has been validated for many hazardous substances in a variety of media.[15–18] The analysis and protocol quality assurance/quality control (QA/QC) requirements have been in use at the U.S. Environmental Protection Agency's (U.S. EPA) Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV) for several years.[1,4,5] The protocol has been shown to be applicable to neutral aprotic, weakly basic and weakly acidic organic compounds which are solvent extractable and boil between 150°C and 500°C.

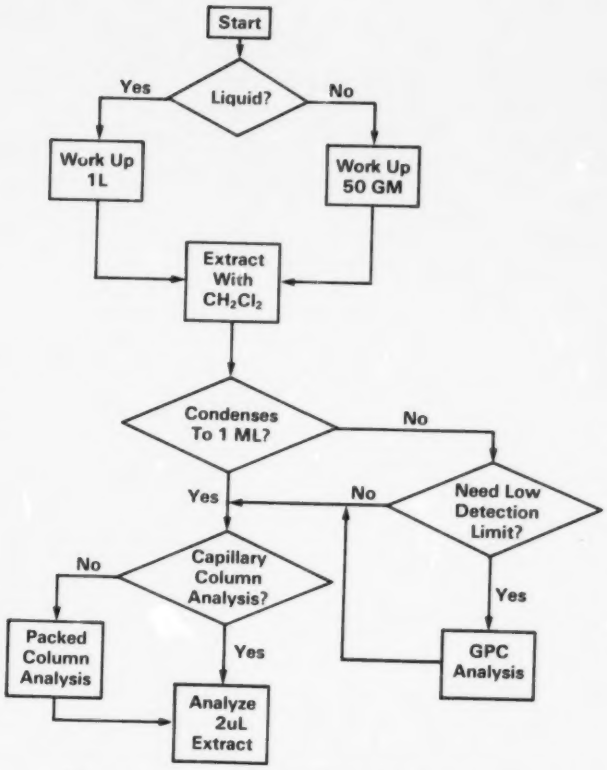

FIG. 1. Protocol sample workup and analysis scheme.

RESULTS AND DISCUSSION

The complete section listings for the protocol are shown in Table I. A complete presentation of the protocol is beyond the scope of this paper. Instead the paper will concern itself with the protocol instrumentation and quality assurance/quality control (QA/QC) requirements, along with expected sensitivity and precision limits. A complete copy of the protocol may be obtained from the author upon request.

The sample workup and analysis scheme for this protocol is outlined in Fig. 1. Sample workup methods were chosen which have been validated for the largest sample sizes (1–2 liters for drinking water and wastewater,[15] and 50 grams for solids).[16–18] This was done to compensate for the insensitivity of the GC/FT-IR technique relative to that of GC/MS. The primary scheme decision points for the analyst are the choice of liquid or solids workup, the desired method detection limits, and the choice of capillary or packed-column GC/FT-IR.

A conservative estimate of the minimum identifiable quantity (MIQ) of 54 environmentally important compounds using on-line GC/FT-IR techniques is listed in Tables II and III. The capillary GC/FT-IR MIQs range from 300 ng for molecules with oxygen-containing func-

TABLE II. Fused-silica capillary-column gas chromatographic/Fourier transform infrared on-line automated identification limits for base-neutral extractables.

Compound	Identification limit, μg	
	Packed[a] column	Capillary[b] column
Isophorone	...	0.30
Nitrobenzene	1.00	0.40
Dimethyl phthalate	1.10	0.40
Diphenyl ether	1.20	...
2,4-Dinitrotoluene	2.00	0.30
N-Nitroso-dimethylamine	2.00	0.30
3-Methyl-2-butanone	2.00	...
1,3-Dichlorobenzene	2.00	0.40
Diethyl phthalate	2.00	0.40
4-Chlorophenylphenyl ether	2.00	0.60
Di-*n*-Butyl phthalate	2.10	0.80
Di-*n*-Propyl phthalate	...	0.40
Butyl benzyl phthalate	...	0.40
2-Methylnaphthalene	...	0.80
1,4-Dichlorobenzene	3.00	0.3
bis-2-Chloroethyl ether	3.00	1.00
Hexachloroethane	3.00	0.40
o-Nitrotoluene	3.30	...
Aniline	3.30	0.40
4-Chloroaniline	...	0.40
2-Nitroaniline	...	0.40
3-Nitroaniline	...	0.40
4-Nitroaniline	...	0.55
1,2,4-Trichlorobenzene	3.50	0.40
n-Valeraldehyde	4.20	...
Naphthalene	5.00	0.40
2-Chloronapthalene	5.00	0.80
2,6-Dinitrotoluene	6.00	0.30
bis-2-Chloro-isopropyl ether	6.00	0.40
bis-2-Chloro-ethoxymethane	6.00	0.40
4-Bromophenylphenyl ether	6.00	0.80
N-Nitroso-di-propylamine	6.00	0.30
N-Nitroso-di-phenylamine	6.00	0.80
Thiophene	6.20	...
1,2-Dichlorobenzene	7.00	0.50
Acenapthene	7.00	...
Acenapthylene	...	0.80
1,3-Hexachlorobutadiene	7.50	0.80
Fluorene	10.00	0.80
Hexachlorocyclopentadiene	10.00	...
Phenanthrene	...	0.80
Benzyl alcohol	...	1.00

[a] Determined on-the-fly using on-column injection and with a 6 ft × ⅛ inch i.d. glass column packed with 1.5% OV-17 and 1.95% OF-1 on 80/100 mesh Gas Chrom Q. A helium flow of 30 mL/min was used and the GC was programmed from 70° to 225° at 10°/min. The interferometer scan rate was 0.3 cm/s and 3 scans/2 s were collected. The lightpipe was gold-coated with dimensions of 60 cm × 2.4 mm i.d. and was maintained at 240°C. A narrow-band HgCdTe detector (3800–700 cm^{-1}) with a 2-mm^2 focal chip was used (5).

[b] Determined on-the-fly using splitless injection and a J & W DB-5 30 M × 0.32 mm fused-silica capillary column (1.0 μm film thickness) at a helium flow of 1 mL/min and using no makeup gas. The GC was programmed from 40° to 280°C at 10°/min. The interferometer scan rate was 1.2 cm/s, and 2 scans per second were collected onto magnetic disk. The lightpipe was gold-coated with dimensions of 12 cm × 1.0 mm i.d. and was maintained at 280°C. A medium-band HgCdTe detector [3800–700 cm^{-1}; D* value (λ peak 1000 Hz, 1) > 1.0 × 10^{10} cm $Hz^{1/2}W^{-1}$] with a 1-mm^2 focal chip was used. These identification limits are a factor of 2.75 better than those reported in Ref. 1 and result from updating the system computer from 32K to 64K of mapped memory and collecting scans to disk rather than magnetic tape.

TABLE III. Fused-silica capillary-column gas chromatographic/Fourier transform infrared on-line automated identification limits for acidic extractables.

No.	Compound	Identification limit, μg[a]
1	Phenol	0.55
2	2-Chlorophenol	0.55
3	2-Cresol	0.55
4	4-Cresol	0.55
5	2-Nitrophenol	0.40
6	Benzoic acid	0.55
7	2,4-Dichlorophenol	0.55
8	4-Chlorophenol	0.95
9	2,4,6-Trichlorophenol	0.95
10	2,4,5-Trichlorophenol	0.95
11	2,4-Dinitrophenol	0.55
12	4,6-Dinitro-2-cresol	0.55

[a] Operating conditions are the same as those cited in footnote b of Table II.

tional groups to 800 ng for the polynuclear aromatics fluorene and phenanthrene. This corresponds to a sample sensitivity of 150 to 400 parts per billion (ppb) for wastewater, if 1 L of water is extracted and the extract concentrated to 1 mL, with 2 μL of extract analyzed. A 50-gram (gm) solid sample undergoing workup by the solids-workup method provides sample sensitivities ranging from 3 to 8 ppm. Note that all MIQs listed in Tables II and III were determined with the use of the same GC program. As a result, the GC peak volumes (elution volumes) of every analyte were not optimized. For example, Gurka *et al.* report a factor of 4.5 difference in GC peak volumes between tetrachloroethylene and di-*n*-Butyl phthalate using the same GC program.[5] Although large GC/FT-IR peak volumes mean reduced sensitivity via analyte dilution, multicomponent analysis necessitates that the elution volume of each analyte cannot be optimized with a single GC run. This resulting sacrifice in sensitivity is made to ensure higher sample throughputs. A further sacrifice in sensitivity was made by the choice of a medium-range mercury-cadmium-telluride (MCT) detector over a narrow-band MCT detector. This choice was made to allow detection of the environmentally important carbon-chlorine and aromatic out-of-plane vibrations.[19]

The minimum identifiable quantities listed in Tables II and III have been obtained with the use of the GC/FT-IR system from the Environmental Monitoring Systems Laboratory, Las Vegas, Nevada (EMSL-LV), which has been described elsewhere[1,4,5] and has recently been updated to include a Data General Nova 4 computer equipped with a high-speed array processor and a Lark Model, Control Data 50 megabyte double-disk drive. GC/FT-IR sensitivity values for strong infrared absorbers ranging between 200 ng for single-beam and 50 ng for double-beam systems have been reported by Griffiths.[20] However, dual-beam GC/FT-IR systems are not commercially available at this time. Recently, Cooper and Taylor have reported identifiable FSCC/GC/FT-IR spectra for as little as 40 ng of some low-boiling compounds.[21,22] At this time the relative sensitivities of GC/FT-IR systems purchased from different manufacturers have not been assessed; however, the MIQs reported in this study have been generated under routine environmental analysis conditions on commercially available instrumentation and should be considered as routinely obtainable.

To establish acceptance criteria for analyte identifi-

TABLE IV. Reproducibility of software-determined GC/FT-IR spectral frequencies.

Compound	ν, CM^{-1} [a,b]	No. runs	No. days	SD[c]
n-Nitroso-dimethylamine	2958.1	14	8	1.70
	1489.0	14	8	0.00
	1476.4	10	7	1.26
	1284.1	13	7	2.40
	1007.9	14	8	1.70
1,3-Dichlorobenzene	1577.4	13	7	1.50
	1454.9	13	7	2.08
	1078.0	10	7	2.11
	783.5	13	7	2.33
1,4-Dichlorobenzene	1476.6	14	7	1.09
	1092.0	14	7	0.00
	1013.5	13	7	1.92
	818.6	13	7	1.50
1,2-Dichlorobenzene	1458.0	13	7	0.00
	1126.3	11	7	2.72
	1036.7	12	7	3.55
	746.5	12	7	1.57
bis-2-Chloroethyl ether	2991.2	9	7	8.39
	1132.6	11	7	2.02
	1088.8	10	7	1.69
	755.3	6	6	3.01
n-Nitroso-di-propyl ether	2974.9	14	8	1.70
	2939.9	14	8	1.38
	2888.8	9	7	3.35
	1484.1	13	8	1.75
	1042.5	13	8	1.13
Nitrobenzene	1540.0	12	8	2.49
	1353.7	12	8	1.15
	852.5	4	4	5.20
Isophorone	2963.0	11	7	0.00
	2904.6	10	7	1.26
	2884.7	7	6	5.62
	1693.6	11	7	1.29
	1372.0	4	3	2.00
bis-2-Chloro-ethoxymethane	2959.0	6	6	3.58
	2892.6	7	7	5.53
	1159.8	10	8	1.93
	1119.6	7	7	4.28
	1033.6	11	8	2.16
Hexachlorobutadiene	1559.1	7	5	1.95
	982.7	9	7	2.00
	853.0	9	7	0.00
	798.9	9	7	1.76
2,6-Dinitrotoluene	1551.4	11	8	1.26
	1357.3	11	8	2.41
2,4-Dinitrotoluene	1605.0	10	8	0.00
	1548.0	13	8	3.00
	1350.0	12	8	0.00
Fluorene	3071.0	10	8	0.00
	1451.3	6	5	2.07
	737.0	8	6	0.00
Di-phenylamine	1595.2	13	8	2.08
	1501.2	13	8	0.83
	1300.0	13	8	0.00
	745.4	7	7	1.13
Phenanthrene	3067.0	10	8	1.89
	805.6	10	7	1.26
	730.5	10	7	2.17

[a] Mean value for the indicated number of runs.
[b] Determined from the peak maximum using Digilab GC/S® software.
[c] Standard deviation for the indicated number of runs.

cation, the author determined the precision of real-time spectral frequencies using the Digilab GC/S® software. This software determines the nominal frequency in cm^{-1} at the peak top of the most intense IR bands within each spectrum. These frequency precisions are listed in Table IV and for sharp IR peaks are ± 1 cm^{-1} or less. Thus, in order for an analyte to be reported as "identified," the frequencies of the major IR bands in the analyte and library spectra should agree to at least ± 1 cm^{-1} and the nominal spectral frequencies for the analyte and library spectra should be determined with the same computer software. (The software used in this study reports frequencies to the nearest whole reciprocal wavenumber. On-the-fly frequency precisions of ± 0.1 cm^{-1} with the use of another manufacturer's software will be reported elsewhere[23]; however, such precision is unnecessary for typical low-resolution environmental measurements.) Acceptance criteria for the relative intensities of the major IR bands in the analyte and library spectra should also be established but at present the necessary computer software is not available.

GC/FT-IR Instrumentation Requirements. The protocol has the following GC/FT-IR instrumentation requirements:

1. Fourier Transform Infrared Spectrometer. A spectrometer capable of collecting at least one scan set per second at 8 cm^{-1} resolution is required. A state-of-the-art A/D convertor is required since it has been shown that the signal-to-noise ratio of single-beam GC/FT-IR systems is A/D convertor limited.[24]
2. GC/FT-IR Interface. The interface should be lightpipe volume-optimized for the selected chromatographic conditions[25] (lightpipe volume about 5 mL for packed columns; lightpipe volume 100–400 μL for capillary columns). The shortest possible inert transfer line (preferably fused silica) should be used to interface the end of the chromatographic column to the lightpipe. If fused-silica capillary columns are employed, the end of the GC column can serve as the transfer line.[26,27]
3. Packed Column 1. For base/neutral compounds and pesticides, a 6-foot glass column (¼ in o.d. × 2 mm i.d.) packed with 3% SP-2250 coated on 100/120 Supelcoport (or equivalent).
4. Packed Column 2. For acids, a 6-foot glass column (¼ in o.d. × 2 mm i.d.) packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport (or equivalent).
5. Capillary Column. A fused-silica DB-5 30 M × 0.32 mm capillary column with 1.0 μm film thickness (or equivalent).
6. Data Acquisition. A computer system dedicated to the GC/FT-IR system to allow for the continuous acquisition of scan sets for a full chromatographic run. Peripheral data storage systems should be available (magnetic tape and/or disk) for the storage of all acquired data. Software should be available to allow for the acquisition and storage of every scan set, to locate the file numbers and transform high S/N scan sets, and to provide a real-time reconstructed chromatogram.
7. Detector. A cryoscopic, medium-band HgCdTe

(MCT) detector with the smallest practical focal area. Typical narrow-band MCT detectors operate from 3800 to 800 cm^{-1} but medium-band MCT detectors can reach 650 cm^{-1}. A 650 cm^{-1} cutoff (or lower) is desirable since it allows the detection of typical carbon-chlorine stretch and aromatic out-of-plane carbon-hydrogen vibrations of environmentally important organo-chlorine and polynuclear aromatic compounds. The MCT D* should be $\geq 2 \times 10^{10}$ $Hz^{1/2}W^{-1}$ (λ peak, 1000 Hz, 1). This MCT sensitivity is close to the theoretical maximum.

8. Lightpipe. Constructed of inert materials, gold-coated, and volume-optimized for the desired chromatographic conditions.
9. Gas Chromatograph. The FT-IR spectrometer should be interfaced to a temperature-programmable gas chromatograph equipped with a Grob-type (or equivalent) purged splitless injection system[27-30] suitable for capillary glass columns *or* an on-column injector system suitable for packed-glass columns. A short, inert, transfer line should interface the gas chromatograph to the FT-IR lightpipe and, if applicable, to the GC detector. Fused-silica GC columns may be directly interfaced to the lightpipe inlet.
10. Dry Purge Gas. If the spectrometer is the purge-type, provisions should be made to provide a suitable continuous source of dry purge-gas to the FT-IR spectrometer. (The effect of purge on sensitivity[31] and identification selectivity[2] has been reported.)

GC/FT-IR Quality Assurance/Quality Control Requirements. Following is the proposed protocol QA/QC requirements. Earlier Grasselli, Griffiths, and Hannah[32] proposed QA/QC requirements for computerized IR instrumentation.

Daily FT-IR Quality Assurance/Quality Control.

1. One-Hundred-Percent Line Test. Set the GC/FT-IR operating conditions to those employed for the Sensitivity Test (see the appropriate protocol section). Collect 16 scans over the entire factor spectral range. Plot the test and measure the peak-to-peak noise between 1800 and 2000 cm^{-1}. This noise should be $\leq 0.15\%$. Store this plot for future reference.
2. Single-Beam Test. With the GC/FT-IR under analysis conditions, collect data for 4 s in the single-beam mode. Plot the coadded file and compare with a subsequent file acquired in the same fashion several minutes later. Note if the spectrometer is at purge equilibrium. Also check the plot for signs of deterioration of the lightpipe windows. Store this plot for future reference.
3. Align Test. With the lightpipe and MCT detector at thermal equilibrium, check the intensity of the centerburst vs. the signal-temperature calibration curve. Signal-intensity deviation from the predicted intensity may mean that lightpipe thermal equilibrium has not yet been achieved, or that there has been a loss of detector coolant, a decrease in source output, or a loss in signal intensity resulting from lightpipe deterioration.
4. Mirror Alignment. Adjust the interferometer mirrors to attain the most stable align interferogram. Data collection should not be initiated until the align interferogram is stable. If necessary, align the mirrors prior to each GC/FT-IR run.
5. Lightpipe. The lightpipe and lightpipe windows should be protected from moisture and other corrosive substances at all times. For this purpose, maintain the light pipe temperature *above* the maximum GC program temperature but *below* its thermal degradation limit. When not in use, maintain the lightpipe temperature slightly above ambient. At all times maintain a flow of dry, inert, carrier gas through the lightpipe.
6. Beamsplitter. If the spectrometer is thermostated, maintain the beamsplitter at a temperature slightly above ambient at all times. If the spectrometer is not thermostated minimize exposure of the beamsplitter to atmospheric water vapor.

Periodic FT-IR Quality Assurance/Quality Control.

1. With an oscilloscope, check the detector centerburst intensity vs. the manufacturer's specifications. For some instrumental sources it is possible to increase the source voltage to meet these specifications; however, this may shorten the source lifetime. For reference purposes, prepare a plot of time vs. detector voltage over at least a 5-day period (see Ref. 23).
2. Frequency Calibration. At the present time, no consensus exists within the spectroscopic community on a suitable wavenumber reference standard for vapor-phase FT-IR. It has been suggested that indene be used as an on-the-fly standard. See Ref. 33 for other vapor-phase IR reference standards.
3. Capillary Column Interface Sensitivity Test. Install a 30 M × 0.32 mm fused-silica capillary column coated with 1.0 μM of DB-5 (or equivalent). Set the lightpipe and transfer lines at 280°C, the injector at 225°C, and the GC detector at 280°C (if used). Under splitless Grob-type injection conditions, inject 400 ng of nitrobenzene, dissolved in methylene chloride, while programming the GC from 40° to 280°C at 10°/min with a carrier gas flow of 1 mL/min. The nitrobenzene should be identified by the on-line library software search within the first five hits (nitrobenzene should be contained within the search library).
4. Packed-Column Interface Sensitivity Test. Install a 6 ft × ⅛ inch glass column packed with 1.5% OV-17 and 1.95% QF-1 on 80/100 mesh Gas Chrom Q (or equivalent). Set the lightpipe at 240°C, transfer lines at 220°C, the injector at 225°C, and the GC detector at 280°C (if used). Inject on-column 1 microgram of nitrobenzene, dissolved in at least 2 μL of methylene chloride, while programming the GC from 70° to 220°C at 10°/min with a carrier gas flow at 30 mL/min. The nitrobenzene should be identified by the on-line library software search within the first five hits (nitrobenzene should be contained within the search library).
5. Checkup By Manufacturers' Servicemen (optional). The spectrometer and interface may be checked by an authorized repairman for conformance to factory specifications.

Initial FT-IR Quality Assurance/Quality Control.

1. Interferometer. If the interferometer is air-driven, adjust the interferometer drive air pressure to manufacturer's specifications.
2. MCT Detector Check. If necessary, install a new source and check the MCT centerburst with an oscilloscope vs. the manufacturer's specifications (if available). Allow at least 5 h of new source operation before data acquisition.
3. Frequency Calibration. See the preceding periodic QA/QC section.
4. Minimum Identifiable Quantities. Using the GC/FT-IR operating parameters specified in Tables II and III (or equivalent), determine the minimum identifiable quantities for the compounds of interest.
5. Sensitivity Check. Determine the sensitivity of the GC/FT-IR interface.
6. Prepare a plot of lightpipe temperature vs. MCT centerburst intensity (in volts or other vertical height units). This plot should span the temperature range between ambient and the lightpipe thermal limit in increments of about 20°C. Use this plot for daily QA/QC (see the appropriate protocol section and Ref. 5). Two protocol reviewers have noted that the suggestions of Griffiths cited in Ref. 9 will eliminate this lightpipe temperature effect, but it will be some time before these suggestions are implemented by FT-IR instrumentation manufacturers.

GC/FT-IR Extract Analysis. The following analysis scheme and analyte indentification criteria is proposed:

1. Analysis. Analyze the methylene chloride extract using the chromatographic conditions specified in the Table II footnotes for packed- or capillary-column interfaces.
2. GC/FT-IR Identification. Visually compare the analyte infrared (IR) spectrum vs. the search library spectrum of the most promising on-line library search hits. Report, as identified, those analytes with IR frequencies for the five (maximum number) most intense IR bands (S/N $\geq$ 5) which are within ± 1.0 cm^{-1} of the corresponding bands in the library spectrum. Choose IR bands which are sharp and well resolved. If the analyte cannot be unequivocally identified, report its chemical functionality. See Table IV for nominal frequency precisions obtained for typical environmental contaminants with the use of the EMSL-LV GC/FT-IR system with Digilab GC/S® software, and the operating conditions listed in footnote b of Table II. The software used to locate spectral peaks should employ the peak "center of gravity" technique.[34] In addition, the IR frequencies of the analyte and library spectra should be determined with the same computer software.
3. GC/FT-IR Confirmation. After visual comparison of the analyte and library spectrum as described in the previous section (the appropriate protocol section) compare the relative retention times (RRT) of the analyte and an authentic standard of the most promising library search hit. The standard and analyte RRT should agree with ± 0.1 RRT units when both are determined at the same chromatographic conditions.

GC/FT-IR Quantitation. Although this protocol is primarily designed to aid GC/MS identification via confirmation, some quantitation guidelines are provided. Although liquid-phase IR quantitation is well documented, little has been reported concerning on-line vapor-phase FT-IR quantitation techniques.[35] The suggested GC/FT-IR quantitation scheme follows:

1. Infrared Reconstructed Chromatogram (IRC) Technique. After analyte identification, construct a standard calibration curve of concentration vs. infrared reconstructed chromatogram peak area spanning at least two orders of concentration magnitude. Choose the working range to bracket the analyte concentration. This method is most practical for repetitive, target compound analyses. If the IRC calibration curve is nonlinear at the concentration level of interest, use quantitation method 2 or 3.
2. Infrared Band Technique. After analyte identification construct a standard calibration curve of concentration vs. infrared band intensity. For this purpose choose an intense, symmetrical and well-resolved IR band. The calibration curve should span at least two orders of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.
3. Supplemental GC Detector Technique. If a GC detector is used in tandem with the FT-IR detector, the following technique may be used: After analyte identification construct a standard calibration curve of concentration vs. integrated peak area. The calibration curve should span at least two orders of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.

CONCLUSIONS AND RECOMMENDATIONS

This analytical protocol is adequate for the identification of environmental contaminants at the mid-ppb to low-ppm range. The principal problem expected in the application of this protocol to environmental samples is expected to be the concentration of solid waste extracts to 1 mL. In cases of this sort, the extract may be cleaned up by gel permeation, or the analyst may settle for higher identification limits.

Computer software is required to determine real-time relative IR peak intensities and IR peak signal-to-noise ratios. This is required to provide relative intensity, as well as frequency precision, acceptance criteria for analyte identification. In addition, a consensus is required from the spectroscopic community on suitable chemical candidates for vapor-phase frequency calibration of the GC/FT-IR system (one reviewer has suggested indene for this role). This concensus should be sought from the Coblentz Society and/or the appropriate ASTM committee.

Finally, with the use of this protocol, the minimum identifiable quantities and on-the-fly frequency precisions of typical environmental contaminants should be

determined in a round-robin study. Ideally this study should employ laboratories equipped with different-model GC/FT-IR systems. This study is necessary because there are currently eleven commercial suppliers of FT-IR spectrometers. If possible, the round-robin study should be coordinated through the appropriate ASTM and/or Coblentz Society Committees. Since it is certain that the state of the art for GC/FT-IR is expected to evolve, it is the intent of the EMSL-LV to update this protocol on approximately a yearly basis.

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This report has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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